

Radiation induced modifications on structural and luminescence properties of LDPE–Na₂SO₄:Sm³⁺ composites by γ -ray

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Abstract

A comparative study on the morphology, structure and luminescence modifications of LDPE–Na₂SO₄:Sm³⁺ composite induced by gamma irradiation was reported for the first time. The composites were irradiated with irradiation doses of 10, 30, and 50 kGy in air at room temperature. Modifications on structural and luminescence properties of LDPE–Na₂SO₄:Sm³⁺ composites were investigated by using several analytical methods. The X-ray diffraction (XRD) patterns revealed that the cross-linking improved the crystallinity of the composites. Scanning electron microscope (SEM) images illustrated the surface modifications of composites induced by irradiation. Results of positron annihilation lifetime spectroscopy (PALS) suggested that gamma irradiation affected the free volumes concentrations in the samples. The photoluminescence (PL) spectra of non-irradiated and irradiated composites consisted of four main peaks at 563, 598, 644 and 706 nm which could be assigned to the ⁴G_{5/2} → ⁶H_J (*J* = 5/2, 7/2, 9/2 and 11/2, respectively) transitions within the 4*f*⁵ electronic configuration of Sm³⁺. Meanwhile, we observed an additional peak

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at about 686 nm in the irradiated composites, owing to the conversion of $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$. Concentrations of the Sm^{2+} centers linearly increased with gamma irradiation doses, which partly accounted for the degradation of PL intensity of Sm^{3+} peaks.

XRD—X-ray diffraction

SEM—Scanning electron microscope

PALS—positron annihilation lifetime spectroscopy

PL—photoluminescence

CIAE—China Institute of Atomic Energy

1. Introduction

Polymer–phosphors composite materials have been considered as a kind of new functional material with the potential applications in light-converting optical devices [1], light-emitting diodes [2], light conversion agricultural films and other outdoor devices. This kind of composite materials have been widely investigated [3-6] because they combine the advantages of both phosphor and polymer into systems, such as the chemical stability and superior processing property from the polymers as well as low-cost and unique luminescent properties from phosphors.

In our previous paper, Sm-doped LDPE–Na₂SO₄ composite materials were successfully synthesized and their morphology, structure and luminescence properties were investigated [7]. However, the service lifetime and performance of many functional composites are highly influenced after processing. It is well known that irradiation of gamma ray may cause the degradation of materials and change the chemical, mechanical and optical properties of materials, which have attracted much attention [8-12]. The polymer absorbed the energy generated by irradiated of gamma ray and cross-linking or chain scission was produced owing to active species such as radicals. The morphology, chemical structure of the polymer and irradiation dose can determine whether the cross-linking or chain scission is the dominating effect of the irradiation. The luminescence reduction mechanism of the samarium ions in the irradiated Na₂SO₄:Sm phosphors had been investigated in our previous letter [13]. However, after incorporating the phosphor particles into the LDPE polymer matrix,

luminescence properties of composites may be related to the structure of free volume and crystalline of composites.

Although much work has been done on the new kind of functional materials, it is necessary to investigate the modifications on structural and luminescence properties of LDPE–Na₂SO₄:Sm³⁺ composite material induced by gamma irradiation. In this work, positron annihilation lifetime spectroscopy has been used to study gamma irradiation effect on the structure information of composites, which might deep our understanding the mechanism of irradiation effects.

2. Experimental

2.1 Materials

High purity powders Na₂SO₄ (99.99%) and SmF₃ (99.99%) were used as the staring materials to prepare the Na₂SO₄:Sm³⁺ phosphor using the melt-mixing method. The LDPE was obtained from Goodfellow (Cambridge, UK). It has a density of 0.922 gcm⁻³ and a melting point of 110 °C.

2.2 Sample preparation

The details of preparation of Na₂SO₄:Sm³⁺ phosphor had already been reported elsewhere [7]. Synthesized samples were powdered again before using them. LDPE–20%Na₂SO₄:Sm³⁺composites were produced by melt-mixing the synthesized Na₂SO₄:Sm³⁺ phosphor powders into LDPE polymer with mass ratio 20% using a Brabender mixer. The mixing temperature was 150 °C and screw speed was kept at 60 rpm for 20 min. The uniformly mixed composites were compressed to slabs at 30 MPa using a curing press at 150 °C. The average thickness was 0.7±0.05 mm. To

prevent contact with air and moisture, all prepared composites were stored in vacuum desiccators.

2.3 Gamma irradiation

The LDPE and composites plates, with a size of $10 \times 10 \text{ mm}^2$, were irradiated by a ^{60}Co Gamma cell at the China Institute of Atomic Energy (CIAE) in air at room temperature. The samples were sealed into plastic vessels and irradiated with irradiation dose of 10, 30, and 50 kGy at a dose rate of 5.0 kGy/h. The non-irradiated LDPE and composite served as the baseline for performance measurements.

2.4 Measurement

2.4.1 X-ray diffraction and Scanning electron microscope measurements

X-ray diffraction (XRD) patterns of the samples were obtained using a D8 X-ray diffractometer, with $\text{CuK}\alpha_1 = 0.1541 \text{ nm}$ radiation operated at 40 kV and 40 mA, at a scan step of 0.02° in 2θ from 10° to 70° . MDI Jade Version 6.5 software was applied to calculate the crystallinity index, which was determined by comparing the areas under crystalline peaks and the amorphous curve [14]. The surface morphologies of the non-irradiated and irradiated samples were observed using a scanning electron microscope (SEM, Zeiss SUPRA 55) with an accelerating voltage of 10 kV. The surfaces of the samples were pre-coated with 4 nm Pt layer in a high vacuum sputter coater (Leica EM SCD 500) to reduce charging before recording the SEM micrographs.

2.4.2 Positron annihilation lifetime spectroscopy (PALS) measurement

From various study it is clear that the free volume change within the polymer greatly affects the structural and optical properties of materials [15]. Positron

annihilation lifetime measurements were carried out in this work with a fast–slow coincidence ORTEC system with a time resolution of 197 ps (full width at half-maximum for the ^{60}Co prompt γ -rays). The two identical pieces of samples were placed on either side of the ^{22}Na positron source, and then this sample-source-sample sandwich was placed between the two detectors to acquire the lifetime spectra. A total of 2×10^6 counts were accumulated for each spectrum to reduce the statistical error in the calculation of lifetimes. The positron annihilation spectra were de-convoluted using the LT-9 software. LT-9 is one of the most popular software for positron lifetime spectra analysis [16]. It de-convolutes the experimental curve from the instruments functions to set apart the physical meaning information, i.e. positron annihilation lifetime and intensity.

2.4.3 Photoluminescence spectra measurement

The PE and PL spectra of the composite materials were measured by using a totally computer-controlled compact system (Horiba Fluorolog spectrofluorometer) at room temperature. A high band-pass glass filter was set in front of the sample to eliminate the influence of scattered excitation light. Samples were excited at 402 nm and emission spectra were observed in the wavelength range of 540-750 nm. Slit widths were fixed at 2 nm for the excitation and emission entrance.

3. Results and discussion

In order to investigate the effects of γ -ray-irradiation on the crystalline structural and relative crystallinity of the LDPE material, XRD analysis was performed. From the XRD patterns shown in the Fig.1, it is apparent that non-irradiated as well as irradiated LDPE present three main crystalline peaks at 2θ of 21.6° , 24.0° and 36.3° which corresponding to the (1 1 0), (2 0 0), and (0 2 0) lattice planes of LDPE [7]. No

obvious position changes can be observed in the XRD patterns after γ -ray-irradiation, which indicates that γ -ray-irradiation at least up to 50 kGy has no significant influence on the lattice parameters of pure LDPE. However, XRD results show that the crystallinity of LDPE increases with the increment of gamma irradiation dose, as shown in Fig.1. This phenomenon may prove that the γ -ray-irradiation mainly causes cross-linking, which takes place in the amorphous region of the LDPE material [17].

Fig.2 demonstrates the XRD patterns for LDPE–20%Na₂SO₄:Sm³⁺ composites irradiated with different doses. The expected diffraction peaks which characterize the Na₂SO₄ crystal (PDF data no.24-1132) in LDPE–20%Na₂SO₄:Sm³⁺ composite [7] are observed in both non-irradiated and irradiated composites. With the increasement of radiation doses in range from 0 kGy to 50 kGy, no significant new peaks are observed. However, the intensity of diffraction peaks varies with the irradiation dose. The change in the intensity of these peaks might be attributed to change in crystalline quality of the composites as a result of gamma irradiation. As shown by XRD results in Fig.2, the crystallinity of composites increases with the increasing radiation dose in range (0-30 kGy), and then decreases slightly at 50 kGy. The reduction in crystallinity of the composite may be ascribed to chain scission at 50kGy. LDPE–20%Na₂SO₄:Sm³⁺ composite has lower crystallinity than the LDPE, which can be explained by that phosphor particles have a strong interaction with LDPE, immobilizing the LDPE chains, giving rise to fewer and smaller crystallites [6].

Fig.3 shows the SEM micrographs for LDPE and LDPE–20%Na₂SO₄:Sm³⁺ composites irradiated with different doses. It can be seen from the Fig.3 (a-d) that the surfaces of both non-irradiated and irradiated LDPE are smooth with no observable discontinuous points. The result indicates that γ -ray-irradiation at least up to 50 kGy has no significant influence on the surface micrographs of LDPE. The SEM images of

LDPE–20%Na₂SO₄:Sm³⁺ composites present the different morphology, in which the surfaces are rougher because of visible Na₂SO₄:Sm³⁺ phosphor particles, as shown in Fig.3 (e–h). The Na₂SO₄:Sm³⁺ phosphor particles are dispersed throughout the polymer matrix with some agglomeration under different irradiation doses. Fig.3 (e) displays that phosphors particles mainly disperse on the surface of polymer matrix in the non-irradiated LDPE–20%Na₂SO₄:Sm³⁺ composites. The SEM micrographs of irradiated composites show that the phosphor particles gradually enter into the polymer networks, which are formed by gamma-irradiation. It may be reasonable to assume that gamma-irradiation leads to the generation of free radicals, and then the free radicals reintegrate to form the polymer networks.

The PALS technique is used to study the size and concentration of free volume cavities in the irradiated pure LDPE and LDPE–20%Na₂SO₄:Sm³⁺ composites. The obtained positron lifetime spectra are resolved into three components using the LT-9 software. The third lifetime (τ_3) with relative intensity (I_3) are due to the pick-off annihilations of orthopositronium in the free volume sites, which exist mainly in the amorphous regions of the polymer matrix. It has been found that τ_3 is proportional to the size of the free volumes and I_3 is proportional to the number of free volumes in polymer. Based on free volume model, Nakanishi et al. [18] have provided the relation between the free volume hole radius (R) and orthopositronium lifetime τ_3 using the following relation

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right]^{-1} \text{ (ns)} \quad (1)$$

where $R_0 = R + \Delta R$, ΔR represents the fitted empirical electron layer thickness, which is equal to 1.66 angstrom. τ_3 and R are expressed in ns and angstrom,

respectively. The free volume radius R has been estimated from the above equation using the values of τ_3 and ΔR . For spherical cavities, the average sizes of the free volume cavities (V_f) are calculated using the following equation

$$V_f = \frac{4\pi R^3}{3} \quad (2)$$

the total free volume fraction (F_v) is proportional to the product $V_f I_3$ and can be expressed as

$$F_v = c V_f I_3 \quad (3)$$

where c is a constant value, which is defined to 10 in this work.

The orthopositronium lifetimes, intensities and corresponding free volume fractions measured in the pure LDPE irradiated with different doses are shown in Table.1. With the increasing of irradiation dose, the o-Ps lifetime τ_3 remains essentially unchanged, the o-Ps intensity I_3 and free volume fraction F_v decrease gradually. The reduction of both I_3 and F_v is corresponding to the reduction of free volume concentration, which seems to fit quite well with the interpretation based on the process of cross-linking [19, 20]. The decrease of free volume fraction F_v is in accordance with the increase of crystallinity, as in Fig.1.

Table.2 reveals the orthopositronium lifetimes, intensities and corresponding free volume fractions of LDPE–20%Na₂SO₄:Sm³⁺ composites irradiated with different doses. As shown by positron annihilation lifetime results, with the increasement of gamma irradiation dose, the free volume fraction decreases with free volume size shrinking at the same time. It is probably attributed to that irradiation-induced cross-linking, which reduces the low-density area of the structure. We can also

consider that the phosphors particles are well incorporated into the LDPE polymer network, which leads to the reduction of the free volume size. This phenomenon is fully consistent with earlier SEM observations.

Optical properties of the matter can be greatly modified by use of irradiation techniques. Samarium-doped materials show relatively stable change in the oxidation state of Sm-ions after exposure to irradiation [13, 21]. The PE and PL spectra of the LDPE–20%Na₂SO₄:Sm³⁺ composites irradiated with different doses are shown in Fig.4. The PE spectra of as-synthesized and γ -ray-irradiated composites monitored at 644 nm show five sharp f – f transition lines, which could be ascribed to the charge-transfer of $^6\text{H}_{5/2} \rightarrow ^4\text{H}_{9/2}$ (345 nm), $^6\text{H}_{5/2} \rightarrow ^4\text{D}_{3/2}$ (362 nm), $^6\text{H}_{5/2} \rightarrow ^6\text{P}_{7/2}$ (375 nm), $^6\text{H}_{5/2} \rightarrow ^4\text{L}_{13/2}$ (402 nm, strongest) and $^6\text{H}_{5/2} \rightarrow ^4\text{P}_{5/2}$ (416 nm), respectively [22]. These peaks have no shift with increase in the irradiation doses up to 50 kGy and their intensities decrease. The PL spectra of all samples obtained under 402 nm excitation, consist of four main peaks at 563, 598, 644 and 706 nm, which can be associated to the transitions of $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$ ($J=5/2, 7/2, 9/2$ and $11/2$, respectively) within the $4f^5$ electronic configuration of Sm³⁺. The PL intensity of these Sm³⁺ peaks decreases with irradiation doses. Meanwhile, we can see an additional band at approximately 686 nm from the irradiated composite material. The emission band is associated to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition within $4f^6$ electronic configuration of Sm²⁺. It is clear that gamma irradiation induces creation of the Sm²⁺ in LDPE–20%Na₂SO₄:Sm³⁺ composites.

Fig. 5 shows the relative PL intensities due to Sm²⁺ and Sm³⁺ of γ -ray-irradiated

composites. Non-irradiated LDPE–20%Na₂SO₄:Sm³⁺ composite does not have any Sm²⁺ ions, as can be seen from Fig.4. Exposure to γ -irradiation, the Sm²⁺ band begins to appear and its PL intensity almost linearly increases, whereas the intensity of the Sm³⁺ line decreases with the increasing of irradiation dose. This feature is mainly ascribed to the conversion from Sm³⁺ to Sm²⁺ in LDPE–20%Na₂SO₄:Sm³⁺ composites. The mechanism can be well explained by that in Na₂SO₄ matrix with γ -ray-irradiation, divalent oxygen anion is changed to monovalent anion by releasing an electron, which will be captured by Sm³⁺ centers [13]. On the other hand, the reduction of the amount of free volume available caused by gamma irradiation, which restricts the mobility of Sm²⁺, can also lead to an increase in emission intensity of Sm²⁺ band [15]. The decrease of luminescence intensity of Sm³⁺ peaks caused by γ -ray-irradiation may affect the PL efficiency of composites. No luminescence of LDPE was detected under the same experimental conditions.

4. Conclusion

The modifications on morphology, structure and luminescence properties of LDPE–20%Na₂SO₄:Sm³⁺ composites induced by gamma irradiation were studied by means of SEM, XRD, PALS and PE, PL spectra. XRD results indicate the crystallinity of samples increases with the increasing irradiation doses. It can be considered that low-dose γ -ray-irradiation mainly causes the cross-linking of LDPE polymer matrix. The PL spectra show that irradiation induces the conversion of Sm³⁺ \rightarrow Sm²⁺ in LDPE–20%Na₂SO₄:Sm³⁺ composite material. Concentrations of the Sm²⁺ centers linearly increase with irradiation doses. The reduction of luminescence

intensity of Sm^{3+} peaks caused by γ -ray-irradiation may reduce the PL efficiency of composites. However, the creation of Sm^{2+} in the irradiated composites may have potential for use in some radiation detection system and other optical devices.

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